Lorentz-Lorenz coefficient and coexistence curve of 1,1-difluorethylene

N. Fameli and D. Balzarini

Department of Physics and Astronomy
University of British Columbia
6224 Agricultural Road
Vancouver, B.C., V6T 1Z1, Canada

Tel: 604-822-4470, FAX 822-5324

e-mail: fameli@physics.ubc.ca
balzarini@physics.ubc.ca

Abstract

The Lorentz-Lorenz coefficient of 1,1-difluoroethylene has been measured as a function of density along the coexistence curve. The density range extends to 1.7 times the critical density. The refractive index is determined by measuring the deviation angle of a laser beam traversing a prism shaped sample. The cell containing the fluid is made from aluminum with windows near one end forming a prism shaped region. The cell has a needle valve for bleeding fluid. The cell is filled with fluid to a high density and placed in a temperature controlled housing. Starting at a temperature at which both liquid and vapour coexist, the temperature is incrementally increased and measurements of the refractive index are made until only one phase exists in the sample. The mass of the sample is then measured. A small amount of fluid is then bled from the cell and the procedure repeated. This is continued until the cell is empty after which the data are analysed obtaining the Lorentz-Lorenz coefficient versus density.

The difference in refractive index of coexisting liquid and vapour phases is measured as a function of temperature. The data are combined with the data from the Lorentz-Lorenz measurements to obtain the coexistence curve.

Key Words: coexistence curve, critical exponents, critical phenomena, Lorentz-Lorenz, polarizability

PACS Nos. 64.60.F

1. INTRODUCTION

The density dependence of the refractive index of 1,1-difluoroethylene ($H_2C{:}CF_2$) has been investigated in order to provide reliable information on the Lorentz-Lorenz relation,

$$L(n,\rho) = \frac{1}{\rho}\frac{n^2 - 1}{n^2 + 2}, \qquad (1)$$

between refractive index, n, and density, ρ, for use in interpreting other experimental data obtained with optical techniques. The substance, $H_2C{:}CF_2$, is also known as Vinylidene Fluoride. It is a colourless, flammable, non-toxic gas at room temperature and atmospheric pressure. Its molecular weight is 64.035 g/mol. Its main use is in preparing polymers and copolymers and as an intermediate in organic synthesis.[1] The material used in this experiment is of 99.4% purity.

Early investigations of the Lorentz-Lorenz coefficient were carried out on pure fluids and mixtures at low densities and generally showed a linear increase with density.[2] Some experiments showed an anomaly near the critical density. These experiments measured refractive index only and required PVT data from other experiments for analysis and interpretation.[3] Correlation of separate experiments can often lead to incorrect conclusions, especially in experiments where we have diverging quantities and where precise temperature control is necessary.

2. EXPERIMENTAL

This experiment consists of measuring the angle of deviation of a collimated laser beam traversing a prism shaped sample. The sample is in a high pressure container with a prism shaped section formed between two sapphire windows. The temperature of the sample is maintained at a chosen temperature. The experimental arrangement is shown schematically in Fig. 1.

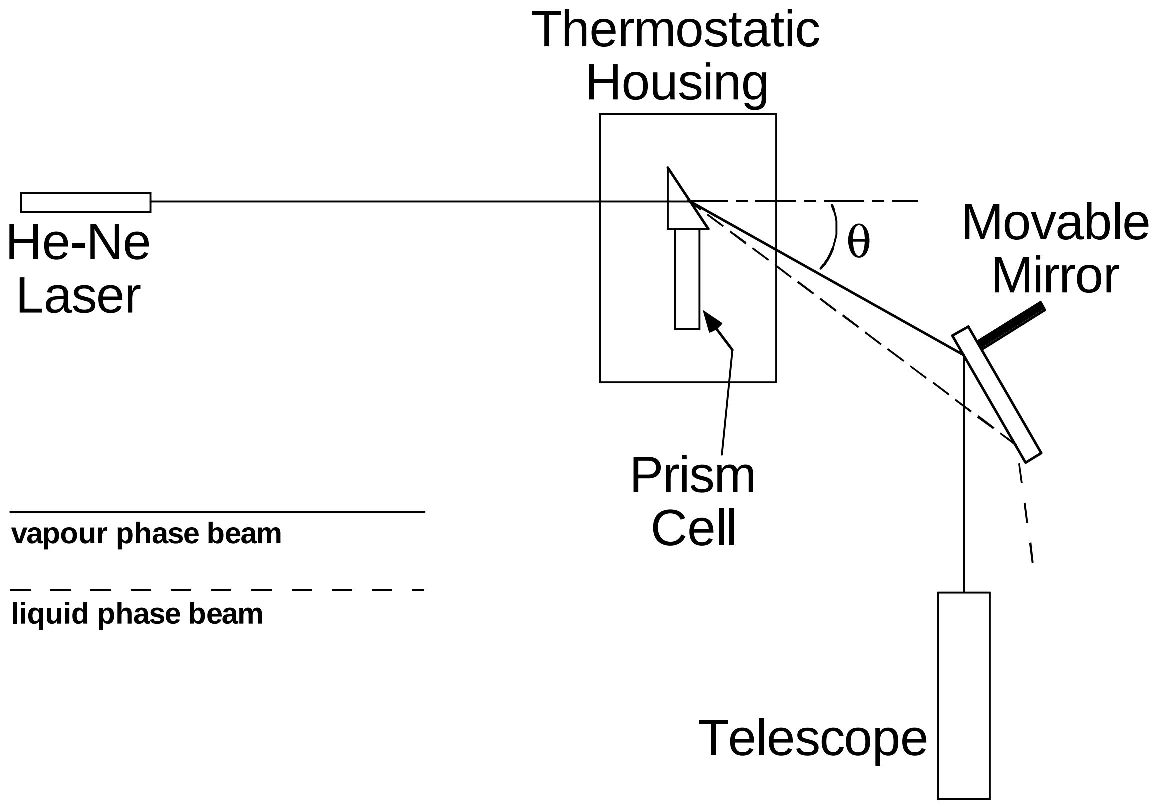

Fig. 1. Schematic diagram of the experimental apparatus.

The sample cell is filled with fluid at a high density and weighed. It is then placed in the thermostatic housing and the angle of deviation of the laser is measured.

The angle of deviation is measured with a micrometer screw on the adjustable mirror which is calibrated by placing a diffraction grating in the position of the sample. If the temperature is such that it is below the coexistence curve, both liquid and vapour phases are present. Since the region of interest is just above the coexistence curve, the temperature is increased incrementally until no further change is measured in the angle of deviation. This corresponds to having the fluid in a single phase. The sample cell is then removed from the thermostatic housing and weighed again. This provides one datum point of deviation angle and sample cell mass.

Some fluid is bled from the sample and the procedure is repeated to provide another measurement. This repetition is continued until the sample cell is empty. This results in a series of measurements of deviation angle versus sample mass. The region over which the measurements are made is shown schematically in Fig. 2 which displays the coexistence curve on a temperature-density graph. The reason for choosing this region is for using the data in interpreting measurements of the coexistence curve from this and other experiments.

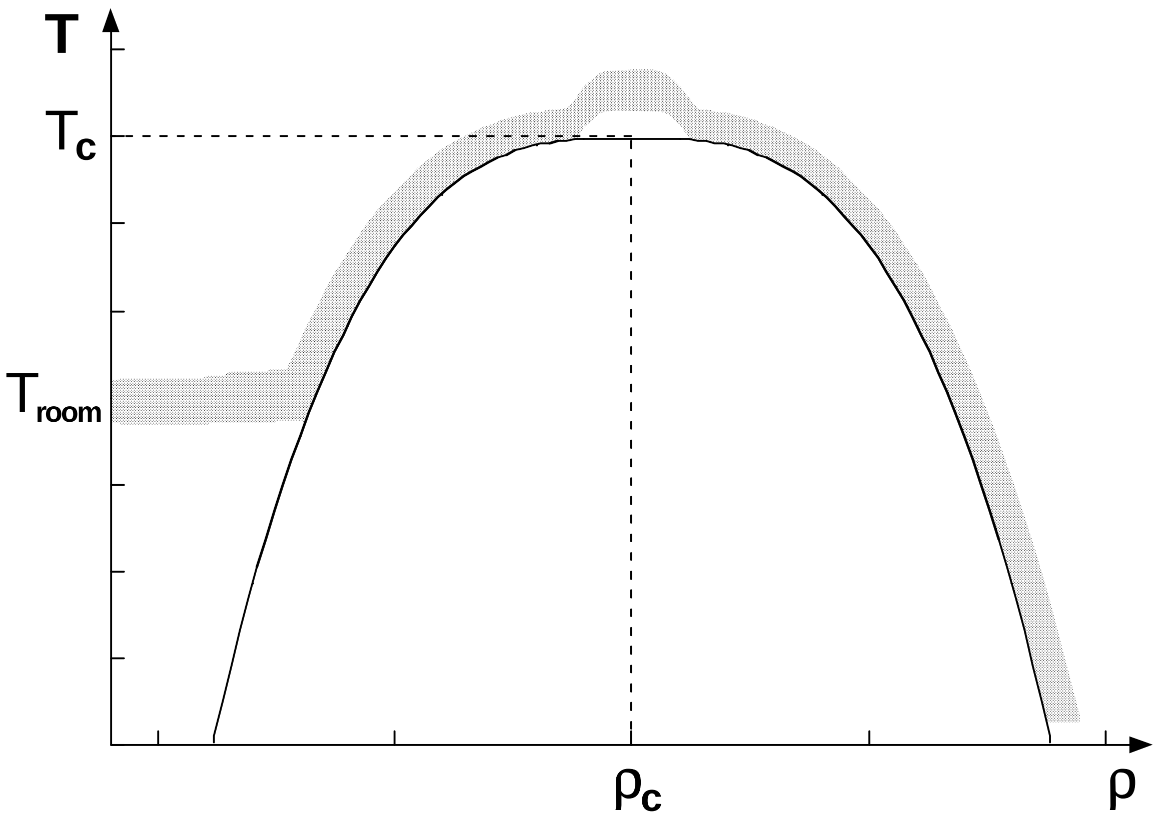

Fig. 2. Schematic illustration of the temperature and density region where the Lorentz-Lorenz coefficient is measured.

The mass measurements are of the sample fluid plus the sample container. The mass of the sample fluid is obtained by subtracting the mass of the empty cell. The index of refraction is obtained from analysis of the optics. Care must be exercised in this analysis in order to eliminate any effects of possible wedge angles in the windows. Any wedges between the sides of the windows were measured at the same time as the internal angle of the hollow prism was measured. The angle of the hollow prism was also measured with high pressure in the cell in order to insure against any significant effects on the experimental measurements. The volume of the sample container is obtained by filling it with distilled water and weighing.

3. RESULTS

The results of the measurements of the Lorentz-Lorenz coefficient versus density are plotted in Fig 3. The value of the L-L coefficient varies by approximately 1% over the density range studied in this experiment reaching a maximum value of approximately 0.1648 cc/g. The uncertainty can be estimated from the scatter of data in the graph to be 0.0002. This variation is consistent with measurements made on other fluids in this lab.[4,5,6] The graph illustrates this variation with density. The data are fitted to an equation of the form,

$$L(\rho)=L_0+L_1\rho+L_2\rho^2+\ldots \qquad (2)$$

The line shown in the graph is a quadratic fit yielding the values of coefficients L_0=0.1576 (cc/g), L_1=0.0267 (cc/g)^2, and L_2=-0.0245 (cc/g)^3.

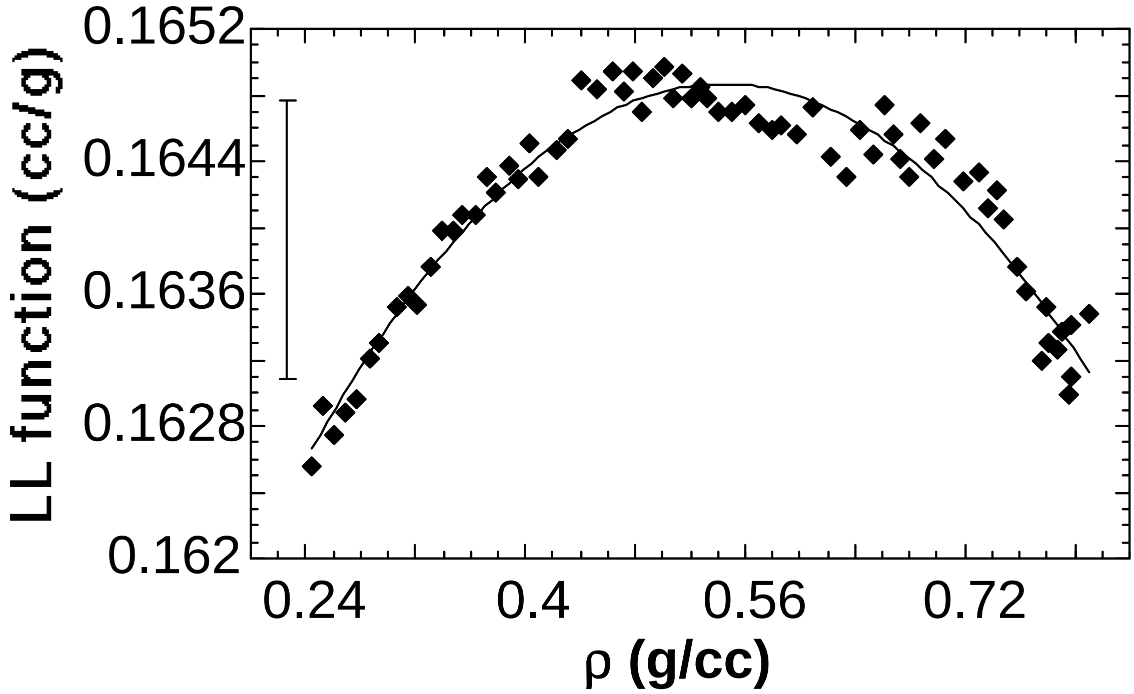

Fig. 3. Lorentz-Lorenz coefficient versus density of 1,1-difluoroethylene.

The coexistence curve is also measured in this experiment. This is done after the sample has been bled to the point corresponding to the critical density. The refractive index of the two coexisting phases can be measured as a function of temperature and analyzed. The coexistence curve data are shown in Fig. 4.

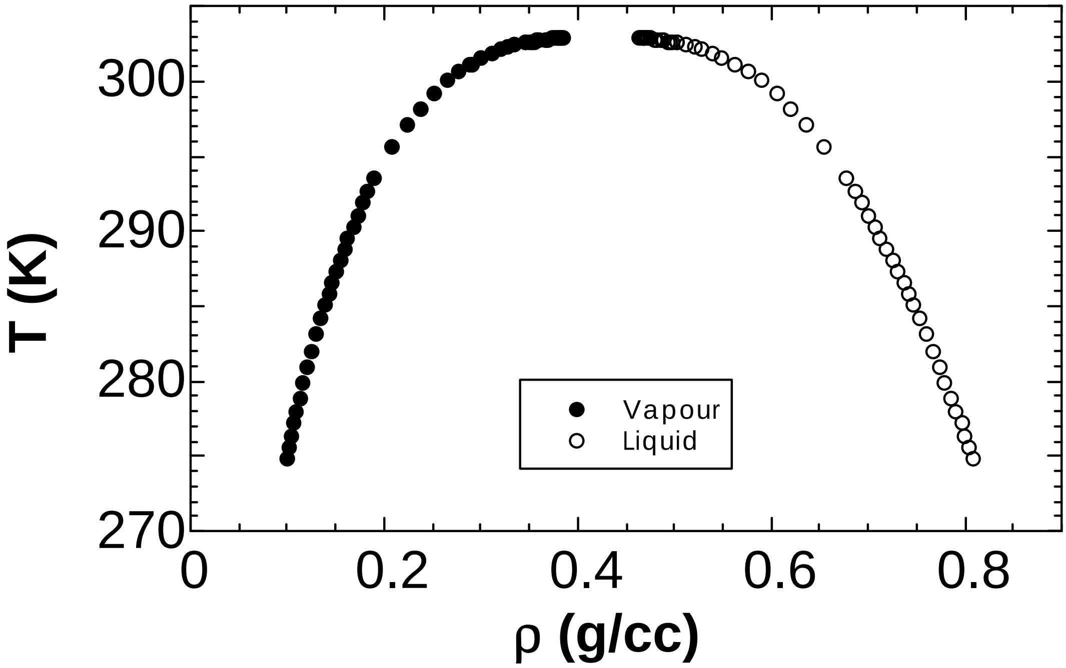

Fig. 4. Coexistence curve of 1,1-difluoroethylene.

The data have been analyzed in terms of renormalization group and scaling theory.[7,8,9] The data are fitted to an equation of the form,

$$\frac{\rho_l - \rho_v}{2\rho_c} = b_0 t^{\beta}(1 + b_1 t^{\Delta} + b_2 t^{2\Delta}), \qquad (3)$$

where t=(1-T/Tc) is the reduced temperature and β and Δ are critical exponents. The data were fit with a standard package for doing non-linear least squares fitting. The results for various parameters are shown in Table I. The parameters in parentheses are held fixed in any fit. The temperature at which coexistence curve data can be obtained is limited as the critical temperature is approached because of the ‘gravitational rounding’ resulting from the increasing compressibility. [11,12]

TABLE I. Parameters of the Coexistence Curve Fits

β	Δ	b_0	b_1	b_2
(0.326)	(0.54)	1.32 ± 0.01	0.50 ± 0.04	(0)
(0.326)	(0.54)	1.393 ± 0.002	0.76 ± 0.02	-1.37 ± 0.07
(0.326)	(0.50)	1.390 ± 0.002	0.68 ± 0.02	-1.06 ± 0.06
0.329 ± 0.002	(0.54)	1.47 ± 0.02	0.21 ± 0.04	(0)
0.328 ± 0.002	(0.50)	1.46 ± 0.02	0.22 ± 0.04	(0)
0.329 ± 0.002	(0.54)	1.430 ± 0.002	0.60 ± 0.02	-1.07 ± 0.06
0.329 ± 0.002	(0.50)	1.425 ± 0.003	0.55 ± 0.02	-0.86 ± 0.06

This research was funded in part by the National Sciences and Engineering Research Council of Canada.

REFERENCES

1. W. BRAKER and A. L. MOSSMAN. Matheson Gas Data Book. 6th ed. Matheson. 1980. pp. 476-480.

2. A. D. BUCKINGHAM and C. GRAHAM. Proc. R. Soc. London A337, 275 (1974)

3. J. M. LUCAS and B. L. SMITH. Phys. Letters 19, 22 (1965).

4. D. BALZARINI and P. PALFFY. Can. J. Phys. 52, 2007 (1974).

5. M. BURTON and D. BALZARINI. Can. J. Phys. 52, 2011 (1974).

6. U. NARGER and D. BALZARINI. Phys. Rev. B 42, 6651 (1990).

7. K. G. WILSON. Phys. Rev. B 4, 3174 and 3184 (1971).

8. F. J. WEGNER. Phys. Rev. B 5, 4529 (1972).

9. M. E. FISHER. In Critical Phenomena Proceedings, RSA 1982. Edited by F. J. Hahne. Springer-Verlag #186. New York. 1983. p. 1.

10. D. A. BALZARINI. Ph.D. Thesis, Columbia University, New York. (1968).

11. M. R. MOLDOVER, J. V. SENGERS. R. W. GAMMON, and R. J. HOCKEN. Rev. Mod. Phys. 51, 79 (1979).